

APPLICATION  
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TITLE: METHOD FOR FABRICATING A BARRIER LAYER  
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### Description

## Method for fabricating a barrier layer

5 The invention relates to a method for fabricating a barrier layer which is suitable in particular for the fabrication of multilayer capacitive structures which have oxygen-rich metal oxide layers having high dielectric constants.

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In MOSFET transistors, improved capacitive control of the conductive channel located under the oxide layer can be achieved by reducing the layer thickness of the gate dielectric or by using dielectric materials having

15 high dielectric constants.

In volatile memory cells, in particular dynamic DRAM memory cells, the storage capacitance of the capacitive memory structures is decreased with increasing miniaturization, with the result that, for compensation, it is necessary to increase the capacitance per unit area or the capacitance per area.

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This is likewise achieved by reducing the thickness of the dielectric layer or by using dielectric materials

25 having high dielectric constants.

Certain metal oxide layers are distinguished by particularly high dielectric constants. Known metal oxides having high dielectric constants are titanium

30 dioxide, tantalum pentoxide or aluminum oxide. Such

35 deposition methods such as sputtering, CVD methods or  
MBE methods, and is subsequently thermally oxidized.

Such metal oxide layers cannot, however, be applied directly on the substrate since, during the thermal oxidation of the metal layer, metal ions penetrate into

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the silicon substrate and form conductive metal silicide compounds which can cause short circuits. Therefore, there must be a barrier layer present between the applied metal layer and the silicon substrate before the metal layer is oxidized to form the metal oxide layer.

Hitherto, a layer made of silicon dioxide below the metal layer has been used as barrier layer. However, such a silicon dioxide barrier layer has the disadvantage that, during oxidation of the metal layer lying above it, the silicon dioxide barrier layer grows into the silicon substrate and is thus widened. The widening of the silicon dioxide layer results in a considerable reduction in the capacitance of the multilayer capacitive structure comprising the metal oxide layer and the underlying silicon dioxide layer.

The object of the present invention, therefore, is to provide a method for fabricating an oxygen-impervious barrier layer which makes it possible to form a capacitive structure with a metal oxide without contaminating the substrate.

The invention provides a method for fabricating a barrier layer having the following steps, namely oxidation of a substrate composed of silicon in order to produce a substrate oxide on the surface of the substrate; production of an oxygen-impervious layer at the interface between the substrate oxide layer and the substrate, the oxygen-impervious layer, as barrier, preventing the formation of metal silicide compounds between applied metal and the substrate silicon; etching of the substrate oxide layer until the underlying oxygen-impervious layer is uncovered.

The method according to the invention affords the advantage that, during the growth of a metal oxide layer on the barrier layer, no oxygen can penetrate

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through the barrier layer and, consequently, no undesirable silicon dioxide layer which reduces the capacitance can be produced between the barrier layer and the substrate.

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In a first embodiment of the fabrication method according to the invention, the oxygen-impervious layer is produced by implanting nitrogen ions into the substrate, the substrate being oxidized in such a way that a substrate oxide layer and an underlying substrate-nitrogen compound as oxygen-impervious layer are formed.

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In an alternative embodiment of the method according to the invention, the oxygen-impervious layer is produced by the substrate oxide produced on the surface of the substrate being exposed to a nitrogen-rich gas in such a way that a substrate-nitrogen compound as oxygen-impervious layer forms at the interface between the substrate oxide and the substrate.

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In this case, the substrate oxide is preferably exposed to a pure nitrogen gas, an NO gas, an N<sub>2</sub>O gas or an NH<sub>3</sub> gas.

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The substrate-nitrogen compound preferably comprises pure silicon nitride.

In a further embodiment, the substrate-nitrogen compound comprises silicon oxynitride.

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In a first embodiment, the substrate oxide layer is etched by wet-chemical etching of the substrate oxide layer.

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In a further embodiment of the method according to the invention, the substrate oxide layer is etched in a dry etching process.

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Preferred embodiments of the method according to the invention are described below with reference to the accompanying drawings in order to elucidate features which are essential to the invention.

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In the figures:

Figures 1a, 1b, 1c show process steps of a first embodiment of the invention's method for fabricating a barrier layer;

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Figures 2a, 2b, 2c show process steps of a second embodiment of the invention's method for fabricating a barrier layer;

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Figures 3a, 3b show process steps for forming a multilayer capacitive structure containing a metal oxide layer having a high dielectric constant.

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Process steps for elucidating a first embodiment of the fabrication method according to the invention can be gathered from Figures 1a, 1b, 1c.

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A silicon dioxide layer 2 is formed on a silicon substrate by thermal oxidation or deposition. Afterward, the silicon dioxide layer 2 formed is exposed to a nitrogen-rich gas. A nitrogen-rich gas is preferably pure nitrogen gas or N<sub>2</sub> gas. As an alternative to this, it is possible to use NO gases, NO<sub>2</sub> gases, NH<sub>3</sub> gases or a gas mixture of such compounds as nitrogen-rich gas. The nitrogen combines with the unsaturated compounds at the interface 3 between the silicon substrate 1 and the silicon dioxide layer 2.

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A substrate-nitrogen compound 4 is thus produced at the interface 3, as can be seen from Figure 1b. The substrate-nitrogen compound preferably comprises pure silicon nitride. As an alternative to this, silicon oxynitride can also be formed as substrate-nitrogen compound, depending on the process parameters. Afterward, the silicon dioxide layer 2 or the substrate oxide layer is etched until the underlying oxygen-impervious layer 4, comprising silicon nitride or silicon oxynitride, is uncovered, and the structure as illustrated in Figure 1c is produced. The silicon dioxide layer 2 is etched either in a wet-chemical etching process or in a dry etching process.

Figures 2a, 2b, 2c show process steps of an alternative embodiment of the invention's method for fabricating a barrier layer.

In this case, firstly nitrogen ions are implanted into the substrate 1 in order to form a nitrogen ion compound in the substrate 1. The nitrogen ions are preferably implanted into the substrate with an acceleration energy of 10 to 20 keV. The distribution of the nitrogen ions is Gaussian. The nitrogen ion distribution is indicated by the reference symbol 5 in Figure 2a.

Afterward, the substrate is oxidized in such a way that a substrate oxide layer 2 and an underlying substrate-nitrogen compound layer 4 as oxygen-impervious layer are formed. In this case, during the oxidation, nitrogen accumulates at the interface between the substrate oxide layer 2 formed and the substrate 1. The layer 4 preferably contains silicon nitride as substrate-nitrogen compound. As an alternative to this, the substrate-nitrogen compound may also be formed by silicon oxynitride.

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Afterward, the substrate oxide 2 or silicon dioxide 2 is removed by means of a dry- or wet-chemical etching process, thereby producing the structure shown in Figure 2c.

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The barrier layer produced by the fabrication method according to the invention is outstandingly suitable for forming a multilayer capacitive structure containing a metal oxide layer.

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For this purpose, as shown in Figure 3a, the structure with the barrier layer 4 that has been produced in Figures 1c, 2c in accordance with the fabrication method according to the invention is coated with a metal layer 6. The metal layer 6 preferably comprises a metal which is simple to oxidize and whose metal oxide has a high dielectric constant. In this case, the metal layer 6 preferably comprises deposited titanium, tantalum or aluminum. The metal layer 6 can be deposited by sputtering, a CVD process or an MBE process.

The metal layer 6 is subsequently thermally oxidized, thereby producing a metal oxide layer 7 on the barrier layer 4, as can be discerned from Figure 3b. In this case, the barrier layer 4 prevents chemical bonding of the metal to the silicon substrate 1, with the result that no undesirable metal silicide compounds can be produced. At the same time, the barrier layer 4 prevents oxygen atoms from penetrating through into the substrate 1 during the fabrication of the oxygen-rich metal oxide 7, with the result that a disturbing layer made of silicon dioxide cannot be produced at the interface 8 between the barrier layer 4 and the substrate 1.

The capacitive structure which is shown in Figure 3b and is produced by means of the fabricated barrier layer 4 has a particularly high capacitance per unit

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area. The reason for this is that, on the one hand, the metal oxide layer 7 itself has a high dielectric constant and, on the other hand, the barrier layer 4 formed comprises silicon nitride or silicon oxynitride, which likewise have a relatively high dielectric constant.

Since a disturbing silicon dioxide layer cannot be formed below the barrier layer 4 that is formed during the growth of the metal oxide layer 7, the total thickness of the capacitive structure is small, as a result of which the capacitance per unit area is likewise increased.

A further advantage of the barrier layer 4 formed according to the invention is that the band gap of silicon nitride or of silicon oxynitride is relatively high, with the result that tunneling currents through the barrier layer 4 are very small. This enables the barrier layer 4 to be made very thin, as a result of which the capacitance of the capacitive structure shown in Figure 3b is increased further.

When the capacitive structure, as is shown in Figure 3b, formed according to the invention is used for constructing memory cells, the small tunneling currents through the barrier layer 4 made of silicon nitride or silicon oxynitride have the effect that the leakage currents of the memory cell are very small and data can thus be stored long-term even in volatile memory cells, for example DRAM.

The silicon dioxide layer 2 used in the fabrication method is only required for the fabrication process. The silicon dioxide layer allows an underlying barrier layer 4 having a minimal thickness to be produced in a highly controlled manner in terms of process engineering.



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The fabrication method according to the invention makes it possible at the same time to integrate metal oxide layers having very high dielectric constants, without violating the high MOS purity standards.

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